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IRON OXIDE-IRON PHOSPHATES AS SOLID ACID CATALYSTS

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A series of iron oxide-iron phosphate (FeFeP) catalysts with various Fe/P ratio were prepared with the coprecipitation method. The acidic properties of these catalysts were examined by temperature-programmed-desorption (TPD) of ammonia and the dehydration reaction of isopropanol. The reaction was carried out in a continuous flow microreactor at 120–230 °C under atmospheric pressure. Alumina-aluminum phosphates (AAPs) were also included in this study. The results of TPD of ammonia indicated that the surface of FeFeP is weakly acidic and their strength are approximately the same. The dehydration activities of these catalysts are decreased with increasing the Fe/P ratios of the samples. Correlation between the reaction rates and the Fe/P ratios indicated that the addition of phosphorus enhanced the acidities of the catalysts.

1. Introduction

The applications of alumina-aluminum phosphate (AAP) catalysts to catalyze the dehydration, isomerization, and rearrangement reactions have been widely reported in the recent years. Because the chemical structure of iron phosphate is similar to that of alumina phosphate, we have undertaken a series of investigations concerning the pore structure and catalytic activities of nonstoichiometric iron phosphate. It has been found that it is a mixture of iron oxide and iron phosphate. Therefore, FeFeP is used to stand for iron oxide-iron phosphate material. Here we report the synthesis of FeFeP by the method of coprecipitation and a study of acidic properties as determined by temperature-programmed-desorption of ammonia. We also studied the dehydration reaction of isopropanol in order to understand the correlation with the acidic properties.

2. Experimental

CATALYST PREPARATION

A strongly acidic solution containing ferric cations and phosphate anions was prepared by dissolving ferric nitrate in distilled water and then adding 85%

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solution of phosphoric acid. A second solution was prepared using 1 : 1 volume mixture of ammonium hydroxide and distilled water. The two solutions were slowly added into a third container of distilled water with the rate of addition controlled in order to maintain a constant pH of 8.00 + 0.02. After the addition of the acidic solution was completed, the reaction mixture was stirred for an additional 10 min. The precipitated FeFeP was then filtered, washed with distilled water and dried overnight at 120 ° C. The over-dried material was calcined at 500 ° C in a muffle furnace for 12 hours.

A series of AAP (alumina-aluminum phosphate) with different Al/P ratios was included for comparison. The preparation of AAP is exactly the same as that reported by Marcelin et al. [1].

A stoichiometric shorthand notation will be used to indicate the atomic ratio of Fe/P or Al/P. For example, the material has a Fe/P atomic ratio of 10 is referred to simply as FeFeP(10).

NH_3 TPD

In a typical experiment, 100 mg of sample in a U-shaped quartz tube was activated at 773 K for 6 hours. After couling to room temperature, high purity ammonia (99.99%) was adsorbed. The temperature was raised and held at 423 K until no physically adsorbed NH_3 was desorbed. The temperature was then automatically raised at 5 ° C/min to 700 ° C under a stream of He at 30 ml/min. Ammonia desorbed from the sample was titrated with amidosulfonic acid using the Radiometer RTS822 automatic titrator. The total acid amount of the sample can be read in the automatic titrator.

ISOPROPANOL DEHYDRATION

In a typical experiment 100 mg of sample, mixed with 200 mg quartz wool in a U-tubed pyrex reactor, was reactivated at 300 ° C for 3 hours. A saturator containing the isopropanol was kept at a constant temperature of 25 ° C. Nitrogen was used as a carrier gas at a constant flow rate of 15 ml/min. The product was sampled by a six-port valve and analyzed by a Shimadzu gas chromatograph (GC-8A) with a thermal conductivity detector. The column was a 3 meters long and packed with 5% Carbowax in 60–100 mesh HMDS-treated acid-wash Chromsorb W.

3. Results and discussions

NH_3 TPD

Because ammonia gas is basic, it can be desorbed on the surface acidic sites of FeFeP compounds. Thus, one can apply TPD to measure the acidic strength of

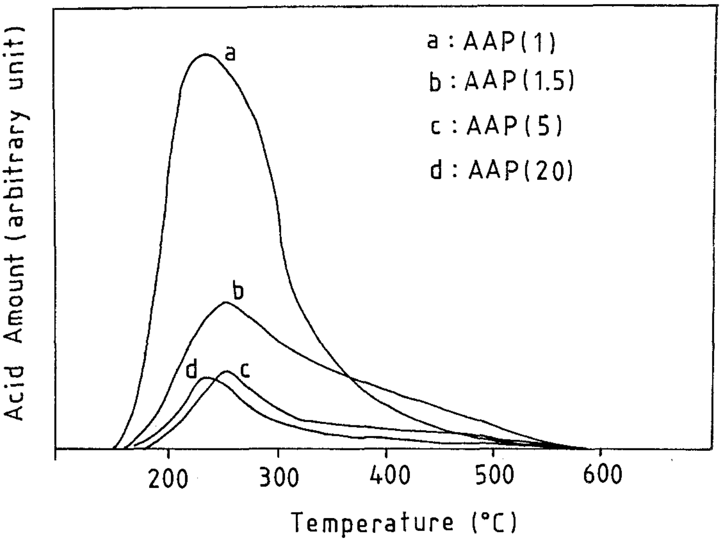

Fig. 1. NH_3 TPD of AAP.

these catalysts, and from the titration amount of desorbed ammonia gas, the surface acidic amount can be determined [2–3]. Fig. 1 shows that the maximum desorption temperatures of AAPs with different Al/P ratios are in the range of 230–250 ° C, and these catalysts belong to medium strength acids. As shown in fig. 2, the $T_{\mathrm{max.}}$ of FeFeP with different Fe/P ratios are also in the vicinity of 230 ° C. Fig. 3 demonstrates that the total acidic amount is closely related to the phosphorus content. In addition under the same phosphorus content, the acidic amount of FeFeP is larger than that of AAP. Campelo et al. [4] reported that the

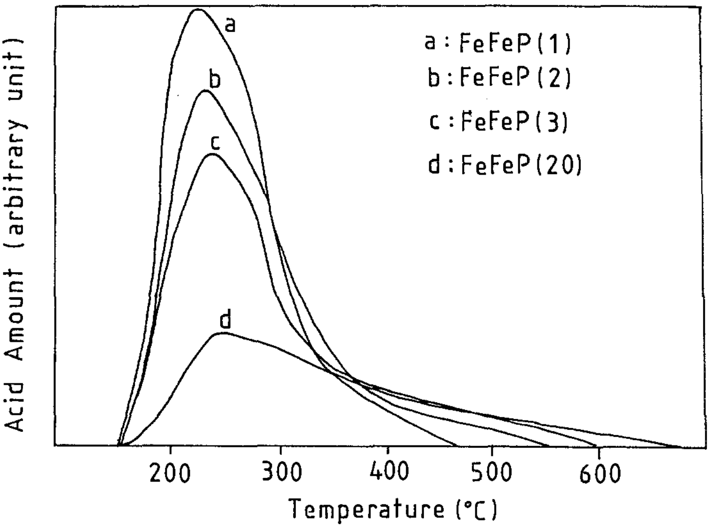

Fig. 2. NH_3 TPD of FeFeP.

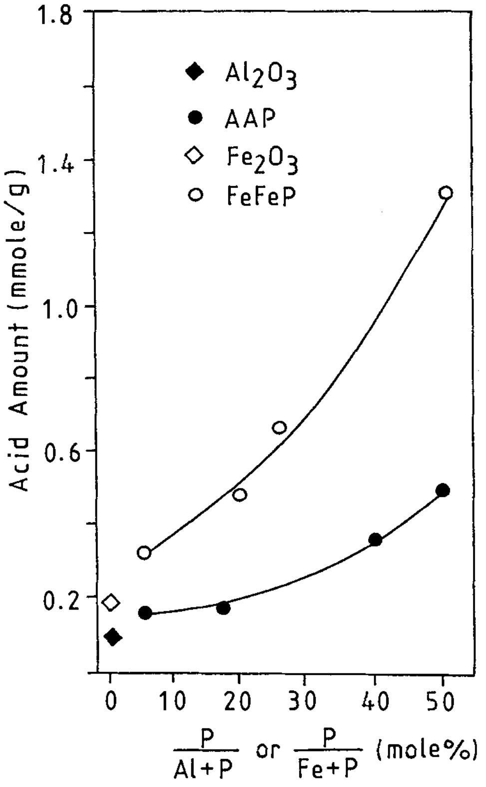

Fig. 3. Acid amount vs. phosphorus content.

surface acidity of AAP is determined by the degree of crystallinity and Al/P ratio. The higher the phosphorus content, the stronger the acidic strength is. Wendt [5] obtained the same results. In this study, we found that the acidic amount of AAP and FeFeP increased with the phosphorus content. However, the effect of phosphorus on the acidic strength is not as dramatic. No distinction is made between Lewis or Bronsted acid sites with this TPD NH_3 method.

ISOPROPANOL DEHYDRATION REACTION

In the isopropanol catalytic reaction, there are two possibilities. One is the electronic effect of dehydrogenation to produce acetone, the other is the acidic effect of dehydration to produce propene and water [6]. The results indicated that isopropanol proceeds simply the dehydration reaction on AAP and FeFeP catalysts. Figs. 4 and 5 show the dehydration activities and acid amount of AAP and FeFeP as a function of phosphorus content, respectively. The results indicated that the reaction activities are mainly decided by the amount of the acidic sites, not by the catalyst acid strength. Murakami et al. [5] also obtained the same results in the acidic cracking reaction over AAP catalysts. The increase in the

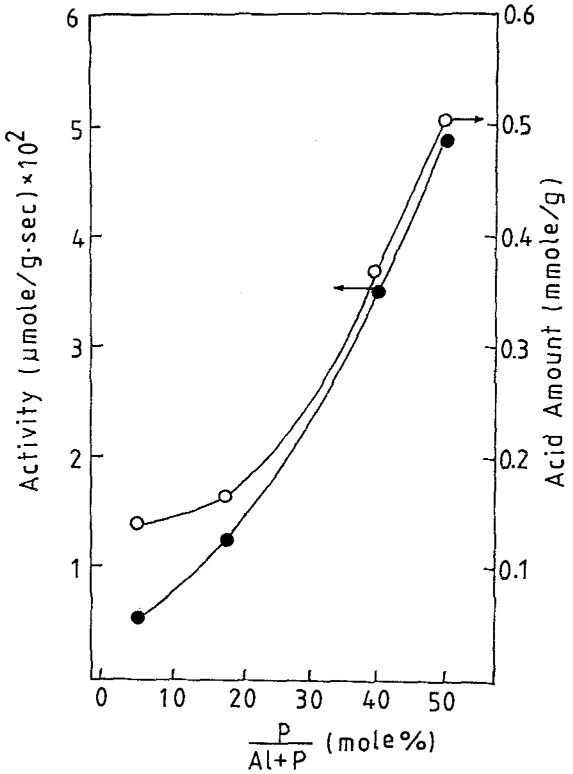

Fig. 4. Isopropanol dehydration activity and acid amount vs. phosphorus content for AAP.

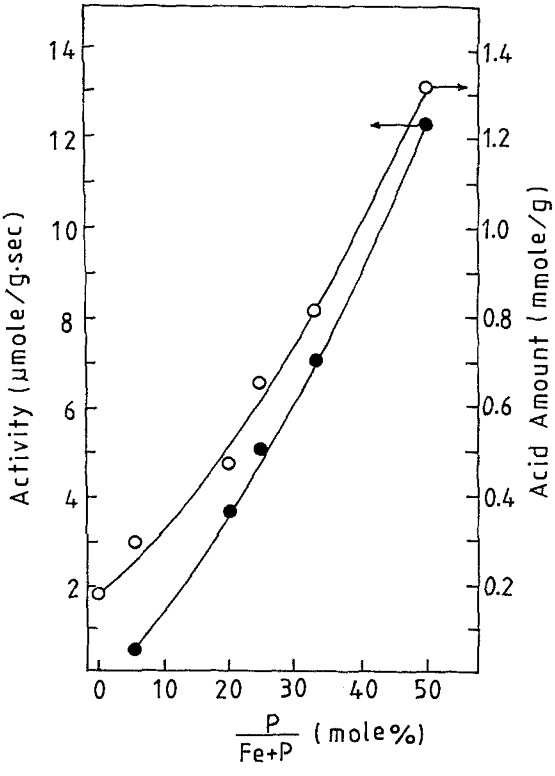

Fig. 5. Isopropanol dehydration activity and acid amount vs. phosphorus content for FeFeP.

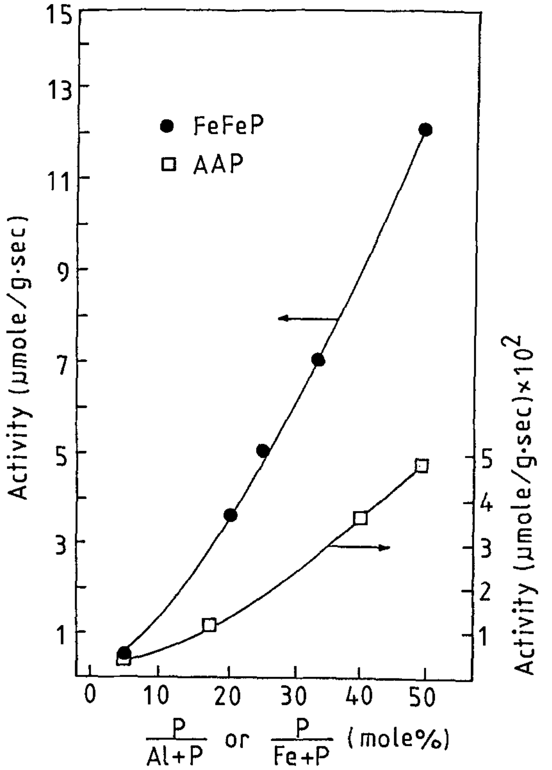

Fig. 6. Isopropanol dehydration activity vs. phosphorus content.

phosphorus content can elevate the concentration of acidic sites, and this would result in the increase of dehydration activities. Fig. 6 shows that the dehydration activities of FeFeP are higher than those of AAPs. This again can be attributed to the larger amount of acidic sites in FeFeP catalysts.

4. Conclusion

A series of FeFeP catalyst with various Fe/P ratio has been prepared via the coprecipitation technique. TPD of NH_3 and isopropanol dehydration reaction have been used to characterize the surface acidities of these catalysts. AAP samples were also included in this study for comparison. TPD of NH_3 results indicated that both FeFeP and AAP belong to medium strength acids. The amount of acid sites is increased with increasing the phosphorus content. In addition, the acidic amount of AAP is smaller than that of FeFeP. The activities of isopropanol dehydration is decreased in the following order: FeFeP > AAP and iron oxide > aluminum oxide. This is essentially due to the different amount of acidic sites, not to the acidic strength of these catalysts.

Acknowledgement

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